

MECHANISM OF "SOLUTION" OF QUARTZ IN PURE WATER AT ELEVATED TEMPERATURES AND PRESSURES*

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ABSTRACT

The solubilities of quartz in pure water at elevated temperatures and pressure are given. Water, under these conditions, differentially etches or corrodes the quartz and gives a solution or suspension that is not homogeneous. It is concluded that silica "dissolves" or disintegrates to give a colloidal suspension.

Quartz crystals contain discontinuities on a different scale. A cementing material of the same composition but of different physical properties from the bulk of the crystal is postulated to exist which holds the various lineage and mosaic elements together. The cementing material is thought to be preferentially removed during etching to produce some of the features observed. Some geological consequences of this argument are given.

A model is suggested to account for both the disintegration and regrowth of quartz.

INTRODUCTION

Conflict still exists in geological and chemical literature over the state in which "dissolved" silica exists in natural waters. Experiments can be cited which indicate that the silica occurs largely as a colloidal dispersion, yet other work seems to point just as clearly toward true solutions.

The physical state in which silica exists in water is of particular interest to geologists in that it has a direct bearing on ideas concerning the breakdown and eventual rebuilding of important rock-forming minerals. Ideas concerning the mechanism of growth of minerals are also involved.

The experiments described in this paper were designed to determine if quartz, when attacked by water, dissolved into individual ions or whether the mechanism of decomposition or disintegration was more complex.

EQUIPMENT

The solubility tests were carried out in two 195 cc. capacity stainless steel bombs, designed by the senior author at Washington University (Fig. 1). The steel used for the body of the bomb was a 100NT-2 alloy developed for jet-turbine blade use in the laboratories of the Massachusetts Institute of Technology under the direction of Nickolas J. Grant (Grant, Frederickson and Taylor, 1948). The other parts were made of various alloy steels possessing different coefficients of expansion so that the parts would shrink free on cooling thus ensuring easy opening

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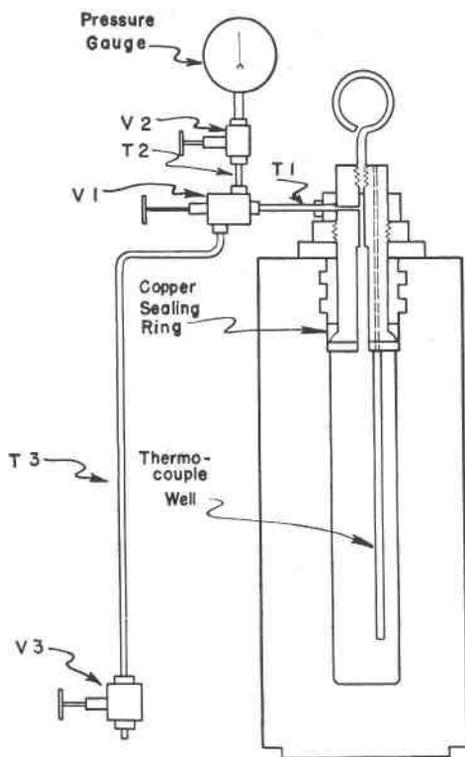


DIAGRAM OF HYDROTHERMAL BOMB
SHOWING TUBE AND VALVE ARRANGEMENT

FIG. 1. Valve V-1 is an offset tee-valve with two connections on the pressure side—one connecting to the bomb head, the other to the isolation valve and pressure gauge. V-2 is the isolation valve, and V-3 the sampling valve for withdrawal of the test solution. By evacuating tube T-3 then closing V-3, valve V-1 can be opened so as to fill T-3 with a known amount of solution. When V-1 is again closed, the test solution is withdrawn into an evacuated flask.

of the bomb. The bombs are designed to give high tensile strength at high temperatures and pressures. Contamination by corrosion within the bomb chamber was eliminated by preheating and quenching the empty bombs so that a durable and inert oxide surface was produced. No metals were detected in a spectrographic check on the solution from the bombs at 370°C ., the maximum temperature used in the tests.

The bombs were heated in electric furnaces, which when closed produced a uniform heating throughout the bomb chamber. Temperature

was controlled to within one degree Centigrade by a Leeds-Northrup controller-recorder, using calibrated chromel-alumel thermocouples. Pressure was produced by the expansion of water with increasing temperature, and controlled by the initial degree of filling of the bomb. Measurements of pressure were made on $4\frac{1}{2}$ " Bourdon-type Ashcroft Laboratory Test Gauges (10,000 psi range) attached to the bombs by isolation valves as shown in Fig. 1. The Bourdon tube of the gauge and the adjoining pressure tubing (T-2, Fig. 1) were vacuum filled with distilled water to eliminate trapped air bubbles, and the isolation valve closed before attachment to the rest of the assembly. In this way pressure in the bomb could be brought to bear on the gauge when desired by opening the isolation valve. The compressibility of the water in the Bourdon tube under these test conditions was considered negligible.

Volume of the system was determined by vacuum filling with distilled water at 20° C. Pressure tubing and valves, suitable for use up to 6,000 psi, were used. The valve and tube arrangement was such that a small amount of solution could be withdrawn during a test without cooling or opening the bomb. (See Fig. 1 and appended explanation.)

PROCEDURE

"Solubility" was determined at two levels in the bomb. One series of tests was made by removing the test solution from the top of the bomb chamber (see Fig. 1). A second series was made in which material from near the bottom of the bomb was sampled through a 5 inch tube welded on to the withdrawal opening of the bomb head. The source crystal of quartz was suspended by a platinum wire about half way between the two points of sampling. The bomb was in an upright position and was not rocked or disturbed during these experiments.

All tests were made at 300 bars pressure. The temperature range covered was from 200° to 370° C. Under these conditions of supercritical pressure and subcritical temperature for water, no gaseous phase existed in the system. The bomb was filled to 88% of capacity with distilled water ($pH=7$) at 20° C., so that when the temperature was raised to 200° C., a pressure of 300 bars would be produced in the bomb. After a previously determined time for establishment of equilibrium under the conditions of each test,¹ withdrawals of aliquots of solution were made. At the temperature and pressure of the first test, three samplings depleted the bomb of enough solution so that the temperature could be raised to 260° C. and the desired pressure of 300 bars maintained. This also provided

¹ In most runs approximately 100 hours elapsed between samplings. This is as much as 3 to 4 times longer than it is necessary for the establishment of equilibrium particularly at the higher temperature where equilibrium is reached in a few hours.

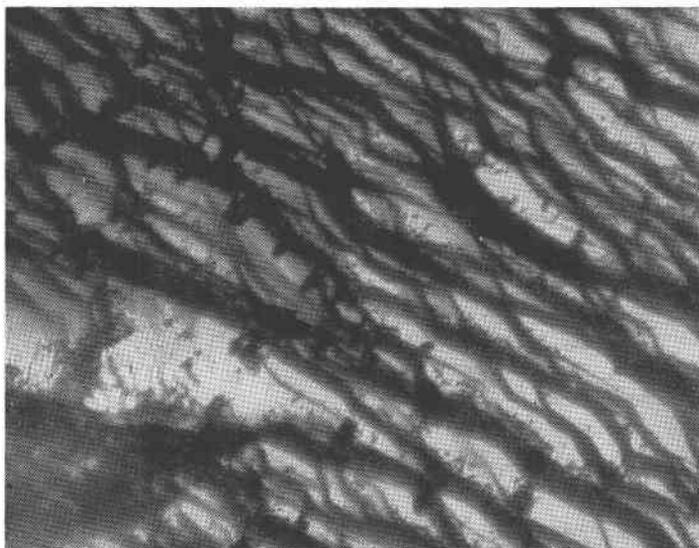


FIG. 2. Regrowth of quartz on the nutrient crystal. Magnification: 80 \times .

The surface of the water-etched quartz crystal has a "shingle" appearance as if it were made up of a series of smaller sheet-like units. The size of the sheets can be seen in the large, irregular protruding fragment in the lower left hand portion of the figure. The small irregular specks along the upper edges of the shingles are quartz that has regrown onto the parent crystal. The black streaks are shadows of the much larger, well-formed quartz crystals which seem to grow most often in the "valleys" between the shingles.

After the last withdrawal was made, the bomb was allowed to cool to room temperature before it was opened. We believe that the smaller quartz crystals along the edges of the shingles grew spontaneously when the bomb was first removed from the furnace. This is equivalent to an air quench. The larger crystals are believed to have developed during the longer cooling period between the time of the air quench and time of opening.

extra portions of test solution as a check. By withdrawing appropriate amounts of solution for each test, the temperature could be raised in steps of approximately 50° and the entire range from 200° to 370° C. covered without opening the bomb.² Each aliquot of solution was placed

² It might be suspected that the temporary pressure drop within the bomb caused by removal of test samples would result in nucleation and formation of particles of colloidal dimensions in the remaining solution. Exploratory runs were made without removing any of the solution, so that the pressure, once established, never fell below 300 bars. The results duplicated those given by the successive withdrawal technique, indicating that in the latter case (1) large nuclei had not been formed immediately on reduction of pressure, or (2) that if formed, they did not survive the temperature increase which followed each withdrawal. This point has a decided bearing on the interpretation of our solubility results, where it becomes necessary to explain a wide difference in solubility between the top and bottom of the bomb, and where the generation and segregation of colloidal sized particles seems to be the most logical answer.

in weighed aluminum foil cups, evaporated and re-weighed to determine the weight of the residue. From this weight and the calculated amount of test solution in the sampling tube at the temperature and pressure of the run, solubility values in parts SiO_2 per hundred parts of water were determined.

This technique permits the operator to actually isolate a portion of the system while it is under the test temperature with only a very small drop in pressure. It is believed that this technique gives more reliable data than quenching methods which give low solubility results because some of the quartz grows back onto the parent crystal before it can be removed from the bomb (Fig. 2).

RESULTS

1. Apparent Solubility Curves

The solubility values are plotted in Fig. 3. The upper curve represents material taken from the bottom of the bomb; the lower curve gives the values for the top of the bomb. The middle curve is drawn through the averages of the two sets of values and indicates the solubility in the bomb

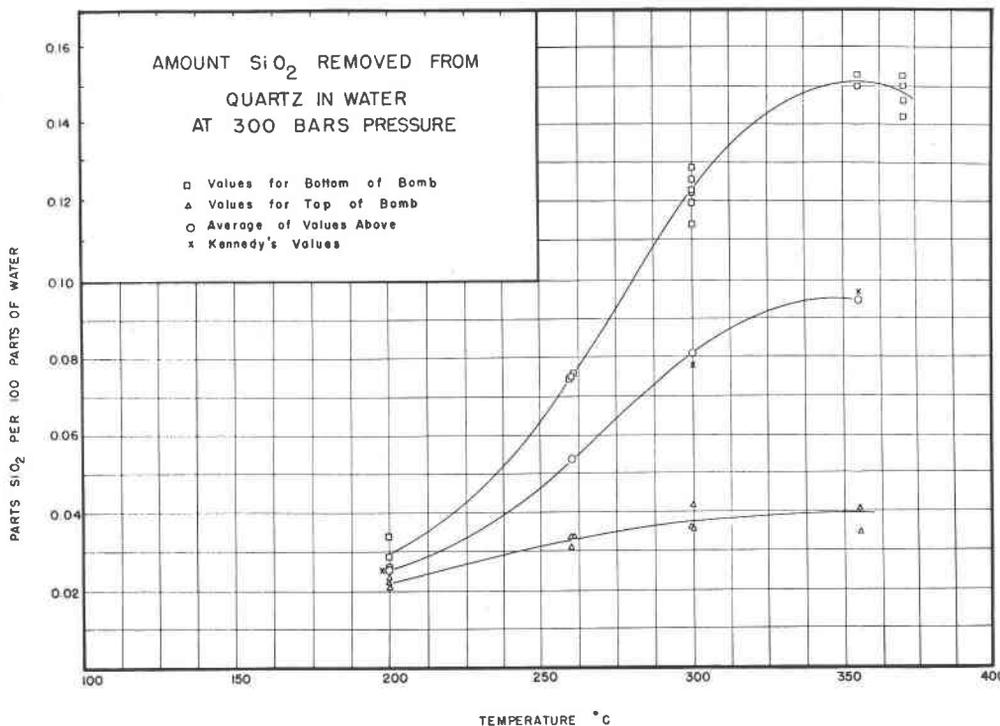


Fig. 3. "Solubility" of quartz in water at elevated temperatures and pressures.

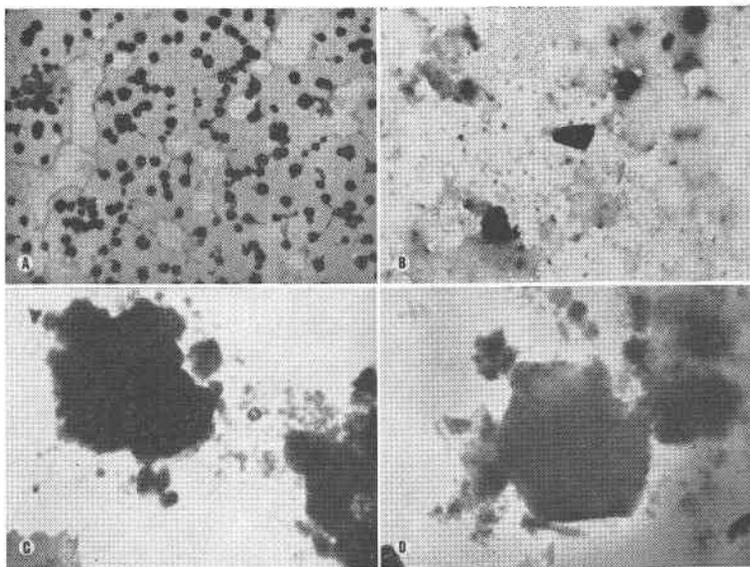


FIG. 4. Electron micrographs of withdrawal products. (From the bottom of the bomb.)

A. Mag.: 2,700 \times . The black spots are believed to be reaggregated silica gel. The gel phase forms a background film which shrinks and cracks on drying. The black spots have a rude polygonal outline which, in many cases, is hexagonal. The uniformity in particle size is remarkable.

B. Mag.: 2,700 \times . A desiccated gel forms the background. The truncated triangular fragment in the center of the micrograph is thought to be a fragment of the parent crystal.

A photographic emulsion cannot record the range in densities that actually exist in the specimen being examined. By varying the printing technique, it is possible to obtain a print that shows quite different apparent results. This fragment did not behave like some others when various tests were applied to it, consequently we believe it to be a solid fragment of the crystal.

C. Mag.: 7,000 \times . Here we see that some of the clumps are aggregates of the gel material. The edges of the clumps are very ragged. Different printing techniques reveal that the clumps are various thicknesses of the gel films and fragments. These clumps are very porous and look much like the first stages of aggregation of many aluminum hydroxide precipitates.

D. Mag.: 8,000 \times . Here is a relatively well formed hexagonal platelet of quartz. It is made up of tiny gel fragments. Each gel fragment is very thin. They often roll up into elongate tube-like particles.

This specimen is an enlargement (made in the electron microscope) of one of the tiny clumps shown in *A*. Apparently all the clumps shown in *A* actually are tiny quartz crystals "in the making."

taken as a whole. For comparison, some points obtained by G. C. Kennedy (1950) using a different technique have been plotted as x's. Note that the averages of the solubility values for top and bottom of the bomb closely correspond to Kennedy's values (1950).

2. *Electron Micrographs of Products*

The products of the decomposition of quartz were examined under an electron microscope. The photomicrographs in Fig. 4 illustrate the range of particle sizes which occur in the solution at room temperature and pressure. The larger masses are re-aggregates and seem to be made up of many chunks of various sizes, most of which are essentially equidimensional. Where some of these fragments have remained dispersed as in photo *A*, they show remarkable uniformity in size and shape, and many have outlines that look suspiciously hexagonal. These crystals are probably aggregates of still smaller particles. Their maximum dimension is 0.27 microns (2,700 Å), whereas the dimension of the average particle in the bomb was calculated to be of the order of 0.08 micron (800 Å). Near these crystals, and extending from them, can be seen traces of a very fine-grained SiO₂ residue left as the droplet of water containing it evaporated.

In photo *D*, the incomplete hexagonal crystal which is taking shape has borders that give a good idea of the size and shape of its building blocks. The length across this aggregate is approximately 2.5 microns. Similar aggregations of various sized particles may be seen in the other photos.

Photos *B* and *C* are typical of the quartz residue in various states of aggregation. The more finely divided material has come out of solution or suspension to produce a patchy film which forms the background in these photomicrographs, and the larger fragments have grouped themselves in clusters.

3. *Electron Micrographic and Petrographic Studies of Quartz Surfaces*

Beyond the evidence given by the two solubility curves (Fig. 3) that "dissolved" quartz exists in different sizes, it is not experimentally possible at present to make a direct determination under test conditions of the actual state of aggregation of the larger sizes in the bomb. A good indirect means of learning something of the suspended particles is to study in detail the surface of the parent quartz crystal which furnished all the SiO₂ to the system. Both the electron and petrographic microscope can be used for this purpose.

Collodian molds or replicas were made for examination under the electron microscope. The replicas were shadowed with chromium according to standard procedure and photographed. Some of the results are shown

in Figs. 5 and 6. The electron micrographs clearly show that the solution action has been preferential even when material is dissolved along the same crystallographic direction.

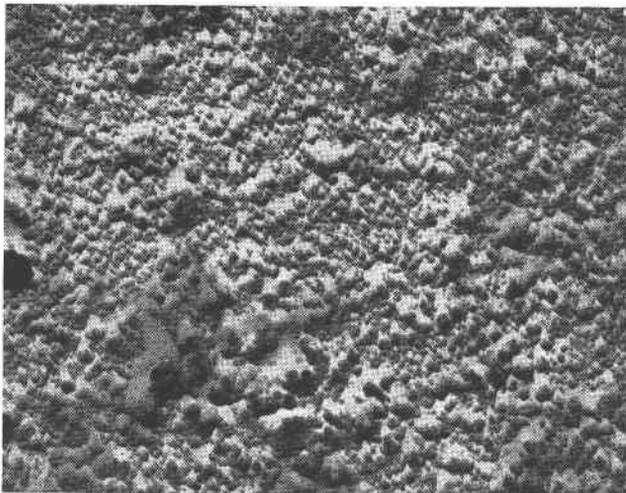


FIG. 5. Electron micrograph of a quartz surface. Chromium-shadowed negative collodian replica. Mag.: 12,000 \times .

The circular elevations on the surface of a water-etched quartz surface are interpreted to represent the ends of resistant rods. The much larger rods or mosaic units shown in Fig. 7D must therefore be made up of smaller units. The similarity in diameter between these circular elevations and the rods shown in electron micrographs of albite (Fig. 6, *Am. Mineral.*, 39, 747, 1954), is striking.

With suitable illumination techniques (Frederickson, 1953a), a considerable amount of detail can be seen on hydrothermally etched quartz crystals. Quartz seems to consist of an aggregate of bundles or elongated fragments (Fig. 7, A, B and C) which, in turn, are made up of smaller elongated units or rods (Fig. 7D).

EVALUATION OF RESULTS AND DISCUSSION

The wide difference in solubility values between the top and bottom of the bomb seems best explained by the segregation of SiO_2 particles—much too large to be considered truly dissolved—from the bulk of the solution and their gradual settling to the lower part of the bomb. The curve for material taken from the top of the bomb is not to be interpreted as truly dissolved silica alone, but includes a considerable amount of colloiddally dispersed silica of smaller particle size than that at the bottom of the bomb.

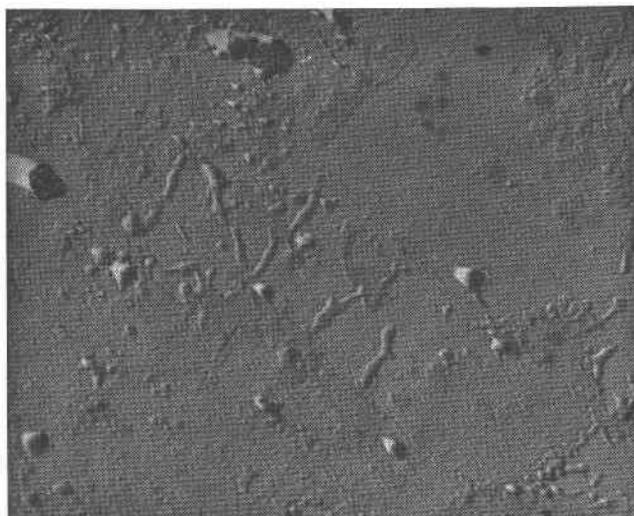


FIG. 6. Electron micrograph of a quartz surface. Chromium-shadowed, negative collodian replica. Mag.: 12,000 \times .

The first stages of etching appears to be a removal of a rather uniform layer. The upper right hand quarter of the micrograph shows a plateau-like surface that has irregular outlines and a few deep furrows and pits. The shadows around the edges of the plateau are quite regular indicating an approximate equal depth of removal of material from the surface. Apparently the attacking solution vigorously corrodes loci of weakness whenever they are encountered to produce pits of various shapes. (The pits here appear as tiny elevations with white shadows because this is a negative replica.)

Something of the nature of the average particle size of "dissolved" quartz in the bomb is given in the following table:

AVERAGES OF CERTAIN CHARACTERISTICS OF "DISSOLVED" QUARTZ

Temperature ° C.	Average Weight in gm/particle	Average Volume Cm ³	Average Number SiO ₂ units/particle
200	1.4×10^{-18}	5.2×10^{-19}	1.4×10^4
260	1.5×10^{-18}	5.5×10^{-19}	1.5×10^4
300	1.7×10^{-18}	6.5×10^{-19}	1.7×10^4
355	2.1×10^{-18}	7.7×10^{-19}	2.1×10^4

Calculations for the above data are based on an equation used in sedimentation equilibrium studies which relates concentration and depth of suspension in a column of water to particle density and volume (Getman, F. H., and Daniels, F.; (1947) *Outlines of Physical Chemistry*).

These tests verify the long standing idea that silica does not exist in dilute water solutions in the form of simple ions. The tests also show that,

at equilibrium under constant temperature-pressure conditions, the silica removed from quartz exists as particles of widely different size; segregation of these particles is demonstrated, and it is suspected that a diffuse stratification of sizes occurs throughout the bomb chamber.

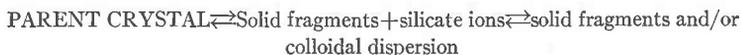
Here two questions arise:

(1) What is the origin of the colloidal sized particles in the bomb—are they flocculates from a true solution of SiO_2 or are they small crystalline fragments removed from the source crystal?

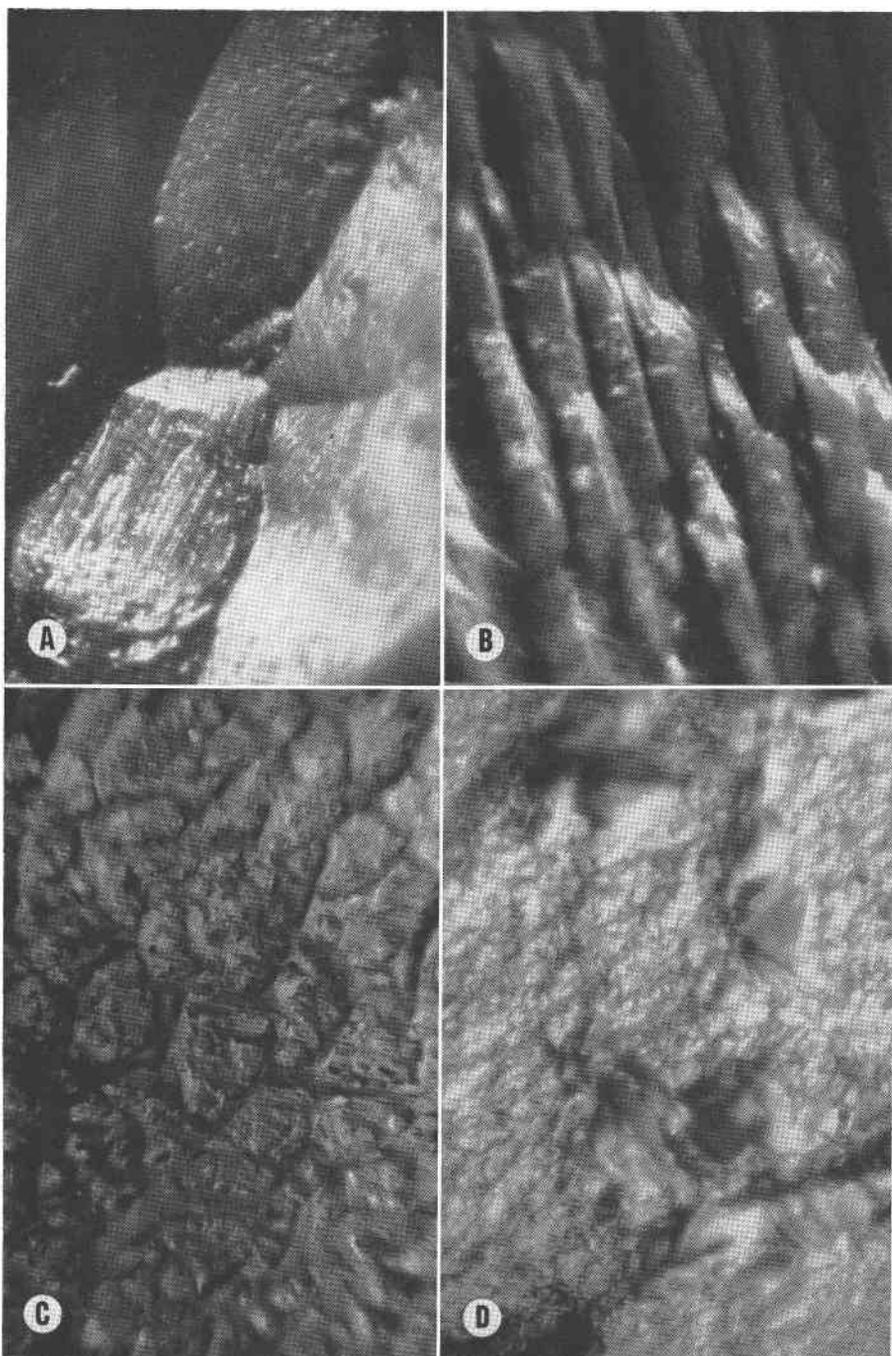
(2) What determines the solubility limit at a given temperature and pressure, and what sort of equilibrium is reached for a silicate mineral such as quartz?

The study of the surface features of the parent quartz crystals showed that along the edges of the stubby to elongated pencil-shaped units that make up the bulk of the crystal, important discontinuities (Fig. 7, *A* and *B*) exist. In addition, when closely examined, quartz appears to have a regular mosaic structure (Frederickson, 1953) the smallest units of which are rod-shaped and are about 0.0009 mm. thick. The length to width ratio averages between 30:1 and 40:1. The rods are laid side-by-side to form sheets or "shingles" so commonly observed on etched quartz surfaces. The sheets are relatively coherent, therefore the rods must be "cemented" or otherwise held together by silica of some kind. Although the larger elongated units are relatively well oriented on a small scale, they show considerable misorientation on a large one. The visible lines produced by this misorientation are called lineages and can be seen in all natural (and synthetically prepared) crystals. Because the crystal, as a whole, has considerable strength, these units must be strongly cemented together. It also follows that this cement that binds the units together must have slightly different properties from the bulk of SiO_2 in the units. If two dendrites or lineage elements start out with a uniform orientation and develop a lineage, the cement must contain a number of bonds at angles different from what is normally found. The cementing material may therefore be considered to exist in a strained or slightly disordered condition and consequently will be more soluble than the units it binds together.

We believe that the equilibrium existing in the bomb can be represented by the following equation:



Under conditions of elevated temperature, the water in the bomb dissociates to form an increased number of hydrogen ions (*I.C.T.*, p. 152,



1929) which attack the weakest oxygen bonds³ in the parent crystal. The weakest bonds in the crystal are found along the lineages and other discontinuities; i.e. in the material we have called the "cement." This results in the formation of silicate ions and the removal of some of the mosaic chunks of quartz from the parent crystal. These chunks enter the solution and, if large enough, settle toward the bottom of the bomb.

The silicate ions do not remain simple but rapidly polymerize to form long, complex ions better termed a silicate polyelectrolyte (Katchalsky, 1950, 1951).

The equilibrium between the solid fragments and the polymerized silicate ions is determined by the temperature of the system which, in turn, controls the number of hydrogens ions available to attack O-O bonds and form new OH bonds.

³ It is a relatively simple matter to imagine how water attacks and dissolves crystals like the feldspars and pyroxenes which contain relatively weak bonds between oxygen and large cations, but in the case of quartz where only O-O or Si-O bonds exist, some reason for the preferential attack of certain of the O-O bonds must be found.

FIG. 7. Photomicrographs of various structures observed on quartz surfaces.

A. Mag.: 180 \times . Irregular shaped masses of quartz separated by important lineage surfaces. Note that these masses are rounded and certainly do not represent any crystallographic surface. These surfaces, then, must be relatively unstable. Deep pits, striations and other irregularities indicate that on this relatively large scale quartz is far from being a homogeneous crystal even though it may show, on a hand specimen scale, relatively perfect crystallographic outlines.

B. Mag.: 225 \times . These are relatively large rods that apparently are made up of the sheets shown in Fig. 2 except that the sheets are broken up by a large number of lineages which are more or less perfectly aligned to give this rod-cluster effect. Here again we see that quartz is very inhomogeneous and that it should not be surprising that it is selectively etched by suitable solvents.

C. Mag.: 90 \times . Water etched irregularities on the surface of quartz crystal which looked perfectly transparent and clear. Spectrographic analyses of these crystals indicated that the amount of contamination was relatively small. Because the whole crystal shows these and the other irregular etch effects shown above, it is highly improbable that substitutions for Si play an important role in the production of weak zones within the crystal which permit it to be selectively etched.

D. Mag.: 150 \times . A quartz oscillator plate, which had been acid etched with HF, was then ground, polished and placed in the bomb for approximately 15 hours. Here we see the very deep pits produced by the HF etch as well as a mottled, rough surface. Within the deep pits can be seen the sheet or shingle structure shown in Fig. 2. Here we see that the sheets are actually made up of a series of small rods held together by some sort of silica cement. The diameter of these rods is very uniform.

The intersections or surfaces of contact of the rods and other irregularities shown in these photomicrographs must be places of weakness in the crystal which can be selectively etched with suitable solvents. Not only is the crystal relatively porous, but when attacked by corrosive solvents (water, for example, under the proper conditions) the quartz crystal may become a veritable molecular sieve. Is it along zones such as these that various cations move when these crystals are part of a metamorphic or other rock?

Although this model has its defects, we think it is essentially correct because it better accounts for our experimental results than any other. It also offers a more rational explanation of certain problems concerning crystal growth. For example, a large patent literature (Stericker and Hazel, 1950) exists on the role played by silica adhesives in systems where it is desired to cement some material (such as phosphors) to glass (television tubes). This analogy has a direct application to the problem at hand.

The silica is introduced into the system in the form of sodium silicate. The cementing process can be described in two steps:

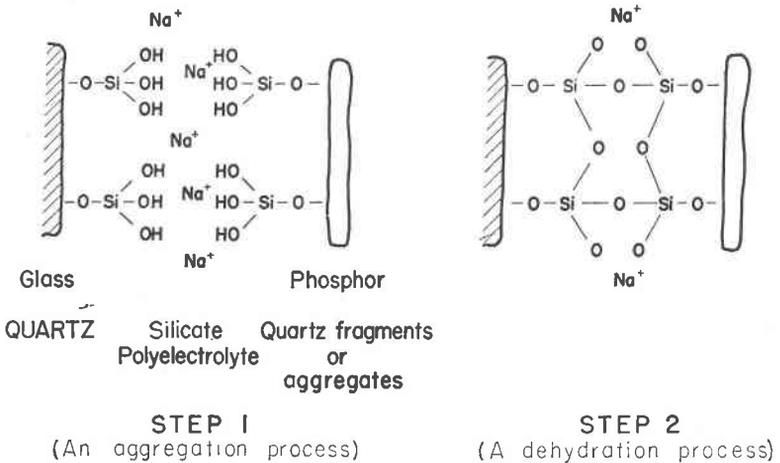


FIG. 8

The silicate in the diagram is simplified to show only one Si^{+4} ion whereas it actually may contain from 5 to 20 or more. Step 1 involves oxygen bond formation by electron sharing between one of the oxygen ions of the silicate and an oxygen on the glass surface. The same reaction occurs between the sodium silicate and the phosphor. The role played by the sodium ions is to bring these two phases, which now possess identical surface charges, into close approach. As soon as the phases are close enough together (flocculation), oxygen-bond formation can again occur as is illustrated in Step 2. This essentially is a dehydration process which releases hydrogen ions which may combine or be shared with oxygen ions to form water. If this reaction is correct (the process works on an industrial scale) we can see why the hydrogen-ion concentration of the starting system is so critical.

Now substitute the words *QUARTZ*, *Silicate polyelectrolyte*, and *quartz*

fragments for those shown in Step 1 of the above diagram and we have the situation which is believed to prevail in the bomb during decomposition of quartz. In the bomb, however, H ions take the place of Na.

The decomposition of quartz results when the hydrogen ions of the water attack the cement to remove mosaic or larger units from the parent crystal. The silicate fragments are in turn attacked by the hydrogen ions and further decompose until the available hydrogen ions are utilized by the silicate polymers and oxygen ions on the surface of the crystalline fragments. Both the fragments (Fig. 4, *A*) and the silicate-polymer (gel) phases (Fig. 4, *A* and *B*) can be directly observed in the electron micrographs of the "solution" siphoned from the bomb. The gel phase results from a more or less complete random polymerization of the silicate when the temperature of the "solution" is rapidly lowered after isolation and extraction from the bomb.

APPLICATION OF THIS MODEL TO QUARTZ SYNTHESIS PROBLEMS

Quartz can be hydrothermally synthesized from a wide range of solutions, the most promising of which are restricted to sodium hydroxide and carbonate. Although very large crystals (up to several pounds) can be made, they are not always as perfect as is desired. The above model suggests that the reverse of the disintegration process might not yield the best crystals. Any crystal fragment may act as a site for development of twins, lineages or other defects. Silicate solutions would therefore appear to be better nutrients than solid quartz maintained in a chamber at a higher temperature than the growing crystal.

If the silicate in solution actually is in the form of large polymers or polyelectrolytes, the initial *pH* and Na-content of the solution will be critical. The degree of openness of the coiled polymers is determined by their degree of ionization and the number of positive ions on the outside of the coil. Addition of positive ions to the coil will cause it to expand or straighten out due to repulsion of the large positive ions along the chain. It is highly probable that optimum crystal growth only occurs when the coiled polymers have the correct surface charge and configuration: they must have a certain degree of openness or uncoiling before they can polymerize to form a *regular* crystal network. If tightly coiled units are dumped onto a crystal surface, it is possible that they might act as sites for the complex twinning often observed.

According to this concept then, twinning, so-called spontaneous nucleation, blue-needle formation and several other kinds of defects are primarily due to sudden changes in the hydrogen-ion concentration of the system induced either by introduction of gasses or sudden temperature changes.

PHYSICAL STATE OF SILICA IN NATURAL DILUTE SOLUTIONS

From a geological point of view, it is important to know whether or not silica in natural waters, under atmospheric conditions, exists as individual simple ions or colloidal complexes. Roy (1945) has recently argued that silica exists as individual ions and not as colloids in natural waters. His best supporting evidence is that during molybdate titrations, silica, in the assumed form of SiO_3^- ions, is precipitated stoichiometrically and that the titration data check gravimetric determinations. Recent work in our laboratories on sodium silicate (Frederickson and Feng, 1953) indicates that, in dilute solution, this material behaves like a large polyelectrolyte and not as a simple ion. This may account for the checks between the titration and gravimetric work without proving that the silicate exists as simple ions.

ACKNOWLEDGMENTS

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